

Traditional and emerging perfluoroalkyl substances in the Cape Fear River Watershed, North Carolina: Occurrence and fate during conventional and advanced water treatment processes

Abstract

Because of their persistence, bioaccumulation potential, and (eco)toxicity, long-chain perfluoroalkyl substances (PFASs) such as perfluorooctanoic acid and perfluorooctane sulfonate are being replaced with short-chain PFASs and fluorinated alternatives. Limited information is available on the occurrence and behavior of these replacement chemicals. The aim of this study was to investigate (1) the occurrence of traditional and emerging PFASs in the Cape Fear River watershed of North Carolina, USA, (2) their fate through a full-scale water treatment plant, and (3) the effectiveness of powered activated carbon (PAC) for their removal by adsorption. In addition to seven perfluorocarboxylic acids (PFCAs) and three perfluorosulfonic acids (PFSAs), seven recently discovered perfluoroalkyl ether carboxylic acids (PFECAs) were studied by liquid chromatography-tandem mass spectrometry (LC-MS/MS). At three surface water intakes, 238 surface water samples were collected from June to November 2013. Concentrations of individual PFCAs and PFSAs reached levels of up to 346 ng/L. Downstream of a PFAS manufacturing site, seven PFECAs were detected. The only PFECA for which an authentic standard was available for quantification, perfluoro-2-propoxypropanoic acid (trade name "GenX"), was detected at an average concentration at 631 ng/L, a level that was approximately five times that of the average summed PFCA and PFSA concentrations (129 ng/L). The remaining PFECAs, were detected but not quantified due to the lack of authentic standards. Among the PFECAs, three exhibited large chromatographic peak areas (up to 15 times the GenX peak area), suggesting possible high concentrations of these emerging compounds. Analysis of samples collected along the treatment train of a drinking water treatment plant with an intake on the Lower Cape Fear River illustrated that neither traditional nor emerging PFASs were removed during coagulation/flocculation/sedimentation, raw and settled water ozonation, biological activated carbon filtration, or disinfection by medium pressure ultraviolet lamps and free chlorine. The adsorption of PFASs by PAC was evaluated with Cape Fear River water samples collected downstream of the PFAS manufacturing facility. Batch tests were conducted with a thermally activated wood-based PAC at doses of 30, 60 and 100 mg/L. The adsorbability of PFASs increased with increasing chain length. PFSAs exhibited a higher affinity for PAC than PFCAs with the same chain length. Replacing one CF₂ group with an ether oxygen atom decreases the affinity of PFASs for PAC, such that mono-ethers of a given chain length have a lower affinity than the corresponding PFCA, but the replacement of additional CF₂ groups with ether oxygen groups did not result in additional affinity changes among the studied PFECAs.

Table S1. PFASs detected in the CFR watershed

| Compound | Formula | Structure | CAS # | Chain length* |
|---|---|---|-------------|---------------|
| Perfluorocarboxylic acids (PFCAs) | | | | |
| Perfluorobutanoic acid (PFBA) | C ₄ HF ₇ O ₂ | CF ₃ (CF ₂) ₂ COOH | 375-22-4 | 4 |
| Perfluoropentanoic acid (PFPeA) | C ₅ HF ₉ O ₂ | CF ₃ (CF ₂) ₃ COOH | 2706-90-3 | 5 |
| Perfluorohexanoic acid (PFHxA) | C ₆ HF ₁₁ O ₂ | CF ₃ (CF ₂) ₄ COOH | 307-24-4 | 6 |
| Perfluoroheptanoic acid (PFHpA) | C ₇ HF ₁₃ O ₂ | CF ₃ (CF ₂) ₅ COOH | 375-85-9 | 7 |
| Perfluorooctanoic acid (PFOA) | C ₈ HF ₁₅ O ₂ | CF ₃ (CF ₂) ₆ COOH | 335-67-1 | 8 |
| Perfluorononanoic acid (PFNA) | C ₉ HF ₁₇ O ₂ | CF ₃ (CF ₂) ₇ COOH | 375-95-1 | 9 |
| Perfluorodecanoic acid (PFDA) | C ₁₀ HF ₁₉ O ₂ | CF ₃ (CF ₂) ₈ COOH | 335-76-2 | 10 |
| Perfluorosulfonic acids (PFSA) | | | | |
| Perfluorobutane sulfonic acid (PFBS) | C ₄ HF ₉ SO ₃ | CF ₃ (CF ₂) ₃ SOH | 29420-49-3 | 5 |
| Perfluorohexane sulfonic acid (PFHxS) | C ₆ HF ₁₃ SO ₃ | CF ₃ (CF ₂) ₅ SOH | 355-46-4 | 7 |
| Perfluorooctane sulfonic acid (PFOS) | C ₈ HF ₁₇ SO ₃ | CF ₃ (CF ₂) ₇ SOH | 111873-33-7 | 9 |
| Perfluoroalkyl ether carboxylic acids with one ether group (mono-ether PFECAs) | | | | |
| Perfluoro-2-methoxyacetic acid (PFMOAA) | C ₃ HF ₅ O ₃ | CF ₃ OCF ₂ COOH | 674-13-5 | 4 |
| Perfluoro-3-methoxypropanoic acid (PFMOPrA) | C ₄ HF ₇ O ₃ | CF ₃ O(CF ₂) ₂ COOH | 377-73-1 | 5 |
| Perfluoro-4-methoxybutanoic acid (PFMOBA) | C ₅ HF ₉ O ₃ | CF ₃ O(CF ₂) ₃ COOH | 863090-89-5 | 6 |
| Perfluoro-2-propoxypropanoic acid (PFPrOPrA or "GenX") | C ₆ HF ₁₁ O ₃ | CF ₃ (CF ₂) ₂ OCF(CF ₃)COOH | 13252-13-6 | 7 |
| Perfluoroalkyl ether carboxylic acids with multiple ether group (multi-ether PFECAs) | | | | |
| Perfluoro(3,5-dioxahexanoic) acid (PFO2HxA) | C ₄ HF ₇ O ₄ | CF ₃ (OCF ₂) ₂ COOH | 39492-88-1 | 6 |
| Perfluoro(3,5,7-trioxaoctanoic) acid (PFO3OA) | C ₅ HF ₉ O ₅ | CF ₃ (OCF ₂) ₃ COOH | 39492-89-2 | 8 |
| Perfluoro(3,5,7,9-tetraoxadecanoic) acid (PFO4DA) | C ₆ HF ₁₁ O ₆ | CF ₃ (OCF ₂) ₄ COOH | 39492-90-5 | 10 |

* Number of carbon (including branched), ether oxygen, and sulfur atoms were added to calculate the chain length.

Commented [DK1]: Add a column for QL? Would be N/A for most ethers

Commented [MS2R1]: Can't do that while keeping the table in the same page. Will see later if they can fit in the materials and methods section

Commented [DK3R1]: OK. Or a separate table for the analytical method that can go into the SI. That table could include information about Q-ions, IS used for quantification, etc.

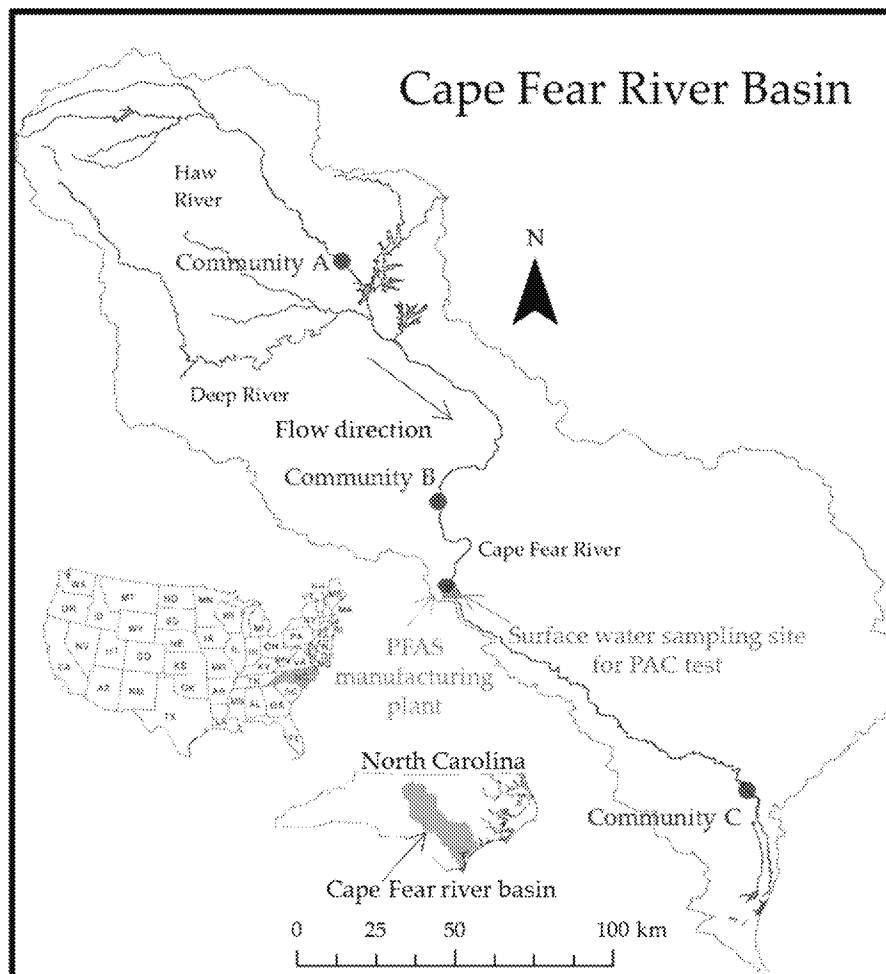


Figure S1. Sampling sites in Cape Fear River watershed, North Carolina

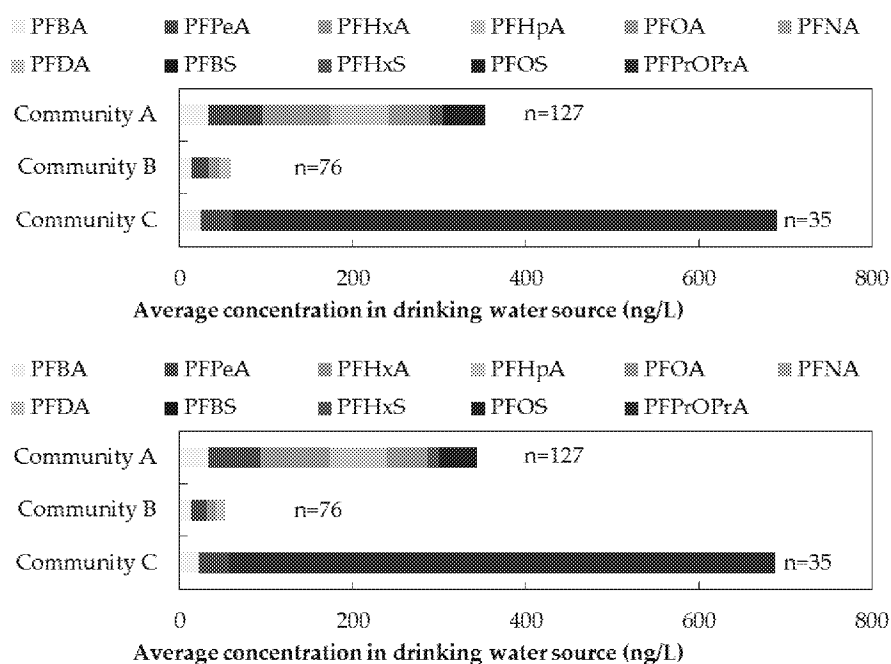


Figure 1. PFAS occurrence at drinking water intakes in the CFR watershed. Concentrations represent averages of samples collected between June and November 2013. Results below the QL were considered as QL/2 (or zero) when calculating averages. Average concentrations less than QL were not plotted. // analyzed by direct injection

Commented [MS4]: The upper figure uses QL/2 for <QL and the lower figure uses zero for <QL in calculating the mean, but not much difference. If the mean is <QL, it is not plotted in either figure.

Commented [DK5R4]: Let's leave both in so Mark and Andy can also comment

- PFASs were detected at surface intakes of three public water systems in the CFR watershed
- In communities A and B, only traditional PFASs were detected (average Σ PFASs at 389 ng/L in community A, and 117 ng/L at community B). The concentrations in community B were lower as a result of dilution by tributaries. One or more important PFAS sources located upstream of community A's intake.
- Max PFOS concentration in community A was above the USEPA drinking water Provisional Health Advisory levels (200 ng/L) on 12 consecutive days during the 127 day sampling. Mean and median concentrations were 49 and 29 ng/L, respectively.
- Mean PFOA concentration in community A (46 ng/L) above New Jersey's guideline to be protective against chronic PFOA exposure (40 ng/L).

- In community C (downstream of a PFAS manufacture site), high concentrations of PFPrOPrA were detected (up to an estimated 4560 ng/L), suggesting the necessity of incorporating emerging PFASs into monitoring. Mean and median concentrations of PFPrOPrA were an order of magnitude higher than those for traditional PFASs in community A. PFPrOPrA concentrations beyond the upper limit of the calibration curve (750 ng/L) were estimated through extrapolation (6 of the 35 samples).

Table S2. Maximum, minimum, mean and median concentrations* (ng/L) of PFASs in CFR watershed surface water as drinking water sources.

Commented [MS6]: The upper table assigned QL/2 to all compound concentration <QL, and the lower table assigned 0. I left the sum line there for reference but could remove in later version.

| | Community A | | | | Community B | | | | Community C | | | |
|------------------|-------------|-----|--------|------|-------------|-----|--------|------|-------------|-----|--------|------|
| | max | min | median | mean | max | min | median | mean | max | min | median | mean |
| PFBA | 99 | <10 | 26 | 33 | 38 | <10 | 12 | 14 | 104 | <10 | 12 | 24 |
| PFPeA | 191 | 14 | 44 | 62 | 38 | <10 | 19 | 19 | 116 | <10 | 30 | 37 |
| PFHxA | 318 | <10 | 48 | 79 | 42 | <10 | <10 | 13 | 24 | <10 | <10 | <10 |
| PFHpA | 324 | <10 | 39 | 68 | 85 | <10 | <10 | 14 | 24 | <10 | <10 | <10 |
| PFOA | 137 | <10 | 34 | 46 | 32 | <10 | <10 | <10 | 17 | <10 | <10 | <10 |
| PFNA | 38 | <10 | <10 | <10 | <10 | <10 | <10 | <10 | <10 | <10 | <10 | <10 |
| PFDA | 35 | <25 | <25 | <25 | <25 | <25 | <25 | <25 | <25 | <25 | <25 | <25 |
| PFBS | 80 | <10 | <10 | <10 | 11 | <10 | <10 | <10 | <10 | <10 | <10 | <10 |
| PFHxS | 193 | <10 | 10 | 16 | 14 | <10 | <10 | <10 | 14 | <10 | <10 | <10 |
| PFOS | 346 | <25 | 29 | 49 | 43 | <25 | <25 | <25 | 40 | <25 | <25 | <25 |
| PFPrOPrA | <10 | <10 | <10 | <10 | 10 | <10 | <10 | <10 | 4560 | 55 | 304 | 631 |
| Σ PFASs** | 1519 | 83 | 241 | 389 | 217 | 70 | 101 | 117 | 4560 | 55 | 304 | 631 |

* Concentrations < QL were considered as QL/2 to calculate means and Σ PFASs.

** Other PFECAs were present in water samples from community C but could not be quantified and were therefor not included in Σ PFASs

| | Community A | | | | Community B | | | | Community C | | | |
|------------------|-------------|-----|--------|------|-------------|-----|--------|------|-------------|-----|--------|------|
| | max | min | median | mean | max | min | median | mean | max | min | median | mean |
| PFBA | 99 | <10 | 26 | 33 | 38 | <10 | 12 | 12 | 104 | <10 | 12 | 22 |
| PFPeA | 191 | 14 | 44 | 62 | 38 | <10 | 19 | 19 | 116 | <10 | 30 | 36 |
| PFHxA | 318 | <10 | 48 | 78 | 42 | <10 | <10 | 11 | 24 | <10 | <10 | <10 |
| PFHpA | 324 | <10 | 39 | 67 | 85 | <10 | <10 | 11 | 24 | <10 | <10 | <10 |
| PFOA | 137 | <10 | 34 | 46 | 32 | <10 | <10 | <10 | 17 | <10 | <10 | <10 |
| PFNA | 38 | <10 | <10 | <10 | <10 | <10 | <10 | <10 | <10 | <10 | <10 | <10 |
| PFDA | 35 | <25 | <25 | <25 | <25 | <25 | <25 | <25 | <25 | <25 | <25 | <25 |
| PFBS | 80 | <10 | <10 | <10 | 11 | <10 | <10 | <10 | <10 | <10 | <10 | <10 |
| PFHxS | 193 | <10 | 10 | 14 | 14 | <10 | <10 | <10 | 14 | <10 | <10 | <10 |
| PFOS | 346 | <25 | 29 | 44 | 43 | <25 | <25 | <25 | 40 | <25 | <25 | <25 |
| PFPrOPrA | <10 | <10 | <10 | <10 | 10 | <10 | <10 | <10 | 4560 | 55 | 304 | 631 |
| Σ PFASs** | 1502 | 18 | 212 | 355 | 189 | 0 | 47 | 62 | 4560 | 55 | 304 | 631 |

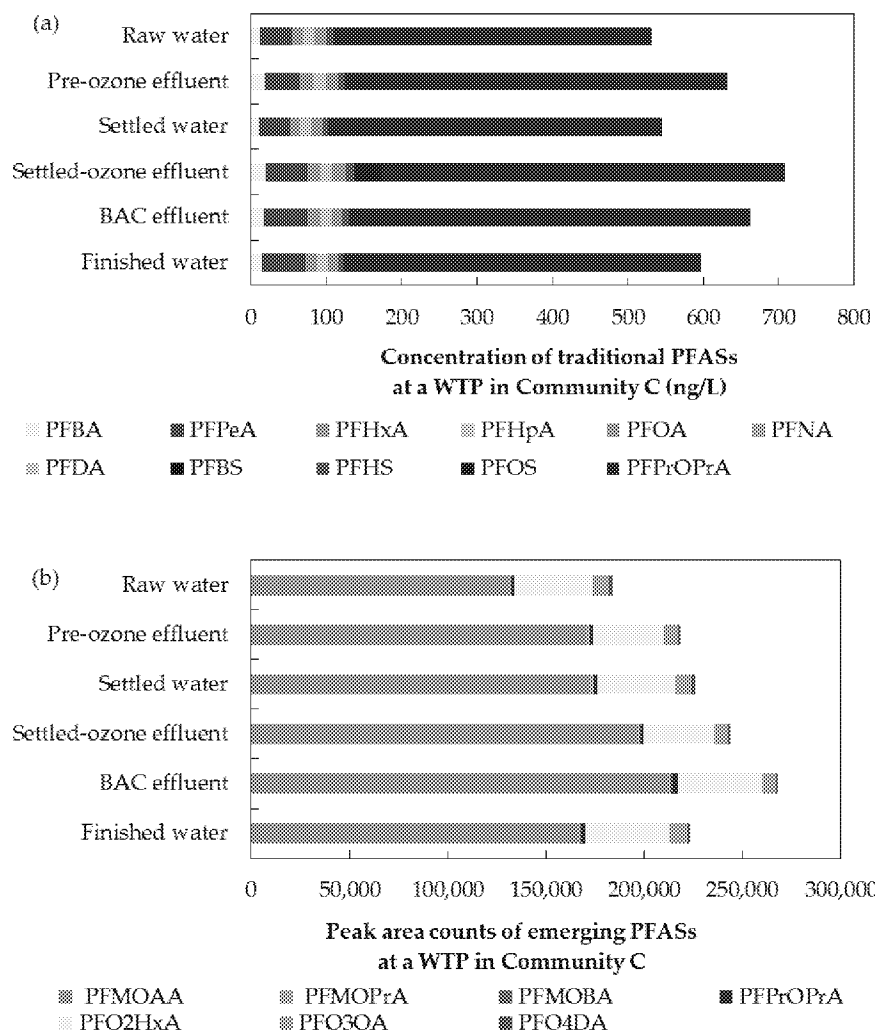


Figure 2. Fate of (a) traditional PFASs and PFPrOPrA and (b) PFECAs through a full-scale water treatment plant. Due to the lack of authentic standards, the emerging PFASs are shown as chromatographic peak area counts from LC-MS/MS analyses. PFPrOPrA data are shown in both figures for reference. [Compounds with concentration less than QL were not plotted. // by SPE - UPLC

Commented [MS7]: The only problem of doing that is all PFOS concentrations are slightly below 25 ng/L except after ozone. Now by removing all <25 values, it looks as if PFOS didn't exist initially but was generated by the ozone treatment...

Commented [DK8R7]: We can explain in the text or caption

- Conventional and several advanced drinking water treatment processes (raw and settled water ozonation, biological activated carbon (BAC) filtration, medium pressure UV disinfection) remove neither traditional PFASs nor fluorinated alternatives
- Ozone may lead to an increase in PFCAs, PFSA, PFMOPrA, PFPrOPrA and PFMOAA concentrations. UV disinfection may decrease concentrations of PFMOAA, PFMOPrA, PFMOBA and PFPrOPrA
- PFPrOPrA is present in both raw and finished water at concentrations that greatly exceeds those of traditional PFASs
- Compared to PFPrOPrA, areas counts for three PFECAs (PFMOAA, PFO2HxA and PFO3OA) were substantially higher.

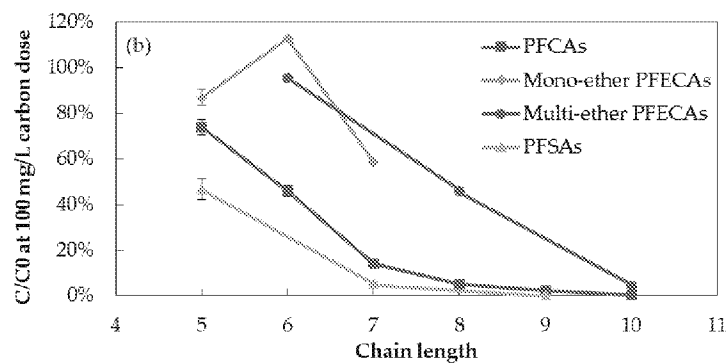
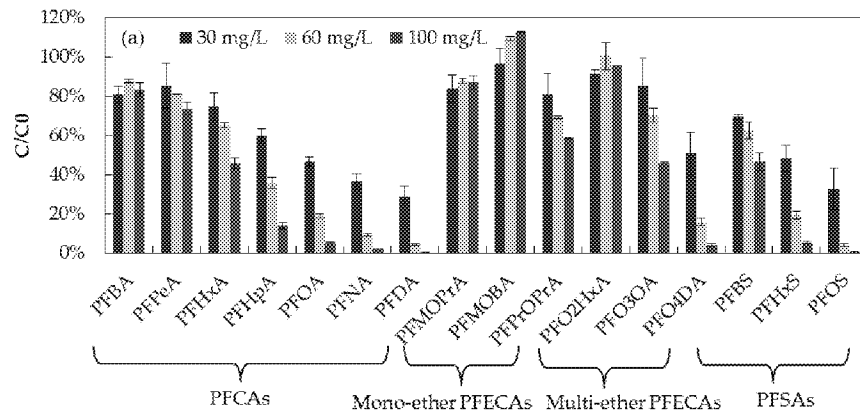


Figure 3. PFAS adsorption to PAC from CFR water after a PAC contact time of 1 hour: fraction remaining (a) at carbon doses of 30, 60 and 100 mg/L and (b) as a function of PFAS chain length. Traditional PFASs were spiked at ~500 ng/L and the emerging PFASs were at their native concentrations. The chart shows the average of remaining PFAS percentage and the error bars show one standard deviation. // by direct injection

- Removals >80% can be achieved with a PAC dose of 100 mg/L for traditional PFECAs with carbon chain length ≥ 7 and with a PAC dose of 60 mg/L carbon for traditional PFECAs with carbon chain length ≥ 8
- At a dose of 100 mg/L, PAC removed 95% of PFO4DA, 54% of PFO3O3, but less than 40% of other PFECAs.
- Adsorbability of both traditional and emerging PFASs increases with increasing chain length
- PFASs were more readily removed than PFECAs of matching chain length
- Replacing one CF_2 group with an ether oxygen atom decreases the affinity of PFASs for PAC, such that mono-ethers of a given chain length have a lower affinity than the corresponding PFCA (e.g. PFHxA vs. PFMOBA). However, the replacement of additional CF_2 groups with ether oxygen groups resulted in small or negligible affinity changes among the studied PFECAs (e.g., PFMOBA vs. PFO2HxA)
- PFECAs have higher affinity to PACs than mono-ether PFECAs with the same number of perfluorinated carbons (e.g., PFPeA vs. PFMOBA), but lower affinity than multi-ether PFECAs with the same number of perfluorinated carbons (e.g., PFPeA vs. PFO3OA)